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Phase Behaviour of Poly(styrene-*co*-methacrylic acid)/Poly(styrene-*co*-*N*,*N*-dimethylacrylamide)/Poly(styrene-*co*-4-vinylpyridine) Ternary Blends by DSC and FTIR

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Summary: we have investigated by DSC and FTIR the miscibility and phase behaviour of binary and ternary blends of different ratios of poly(styrene-*co*-methacrylic acid) containing 15 mol% of methacrylic acid (SMA15) with poly(styrene-*co*-N,N-dimethylacrylamide) containing 17 mol% of N,N,-dimethylacrylamide (SAD-17) and poly(styrene-*co*-4-vinylpyridine) containing 15 mol% of 4-vinylpyridine. SMA15 is miscible with both SAD17 and S4VP15 and interacts more strongly with S4VP15 than with SAD17 as evidenced by the positive deviations from linear average line observed with these blends and the appearance of new bands in the 1800–1550 cm^{-1} region. This behaviour is known as ΔK effect. The FTIR study confirms that though the specific intermolecular interactions that occurred with each pair of the SMA15/S4VP15 and SMA15/SAD17 binary components are of different strength, they still exist in the ternary blend. Even though the three binary polymer pairs are individually miscible, the ternary system of SMA15/S4VP15/SAD17 exhibits only partial miscibility with small loop of immiscibility due to a significant ΔK effect. These results obtained by DSC and FTIR are in a fair agreement with theoretical prediction applying the Painter-Coleman association model.

Keywords: DSC; FTIR spectroscopy; poly(styrene-*co*-4-vinylpyridine); poly(styrene-*co*-methacrylic acid); poly(styrene-*co*-*N*,*N*-dimethylacrylamide); ternary blend

Introduction

It is well known that most polymer pairs do not mix in the absence of specific interactions. The introduction of hydrogen bonding between the two constituents of the blend is now a known method used to enhance the miscibility of pairs of polymers initially immiscible and increasing number of miscible binary polymer blends are reported.[1–4] Though ternary miscible polymer blends offer many opportunities to elaborate new polymer materials with improved properties, based on recent studies,[5–9] only few ternary polymer blends have been reported to be truly miscible over the entire range of composition in comparison to binary blends.

It has been reported by Jo *et al.*[6] that ternary blends of poly(hydroxyl ether of bisphenol A) /PMMA/PEO, composed of three miscible binary blends showed a closed immiscibility loop phase diagram. Similar observations were also reported by Chang *et al.*[7] and by W.P.Hsu[8] in their studies of the ternary phenolic resin PEO/PCL and the PMMA/PVPh/poly(vinyl cinnamate) blends, respectively. An unusual completely miscible ternary blend of phenolic/phenoxy/PCL was recently reported.[9]

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Coleman and Painter[10] stated that because of the $\Delta\chi$ and ΔK effects, truly miscible ternary blends are obtained only in very limited cases where these two effects are finely balanced. The first part of this work is an attempt to dilute the interactions that occurred between poly(methacrylic acid) PMA with poly(4-vinylpyridine) P4VP and poly(methacrylic acid) with poly(N,N-dimethylacrylamide) PDMA that led to their complexation, by introduction of relatively high amounts of styrene moieties within these interacting polymers. The specific interactions that occurred between each binary miscible blend and the phase behaviour of their ternary blends were investigated by DSC and FTIR spectroscopy. Theoretical prediction of the phase behaviour of the SMA15/S4VP15/SAD17 ternary system was performed using the Painter-Coleman association model.

Synthesis and Characterization of Copolymers

Poly(styrene-*co*-methacrylic acid) containing 15 mol% of methacrylic acid (SMA15), poly(styrene-*co*-4-vinylpyridine) containing 15 mol% of 4-vinylpyridine (S4VP15) and poly(styrene-*co*-N,N-dimethylacrylamide) containing 17 mol% of N,N-dimethylacrylamide (SAD17) were prepared by free radical polymerization using azo-bis-isobutyronitrile as initiator at 60 °C. They were then purified by dissolution/precipitation and dried under vacuum at 60 °C for several days. They were characterized in a similar way as previously described[4] by UV spectroscopy and proton NMR. The average molecular weights of these copolymers were determined by GPC using a Perkin Elmer 1100 HPLC. The copolymer characteristics are listed in Table 1.

Table 1.
Polymer characteristics.

Copolymers	Styrene content	M_w	M_w/M_n	Tg
	mol%	Kg.mol^{-1}		K
SMA15	85	65.55	2.74	410
S4VP15	85	06.62	2.98	377
SAD17	83	12.26	2.84	379

Thermal Analyses

The thermal stability of the as-cast copolymers was checked by TGA. These copolymers were stable up to 350 °C, as displayed from their TGA and *d*TGA curves in Figure 1, determined using a Mettler Toledo 851^e at a heating rate of 10 °C/min under nitrogen flow.

Films of binary SMA15/S4VP15, SMA15/SAD17, S4VP15/SAD17 and ternary SMA15/S4VP15/SAD17 blends were prepared by casting from THF solutions with evaporation of solvent.

The glass transition temperature T_g of these copolymers and of their binary and ternary blends of different ratios was measured using Mettler Toledo 821^e DSC, at a heating rate of 20 °C/min. Since these polymers contain hydrophilic groups and in order to minimize water absorption, they were accordingly kept under reduced pressure in a vacuum oven at 60 °C for several days prior to their use. All the thermograms recorded during the second heating scan were considered to obtain the T_g values.

FTIR Measurements

Thin films of SMA15, S4VP15 and SAD17 copolymers and of their binary SMA15/S4VP15, SMA15/SAD17, S4VP15/SAD17 and ternary SMA15/S4VP15/SAD17 blends of different ratios for FTIR measurements were prepared by casting from a 2–3% w/v solution in THF onto KBr disks. The solvent was first evaporated at room temperature. In a similar way as with DSC, the disks were then dried in vacuum oven at 60 °C for several days. Infrared spectra were recorded at room temperature on a SHIMADZU FTIR spectrometer with

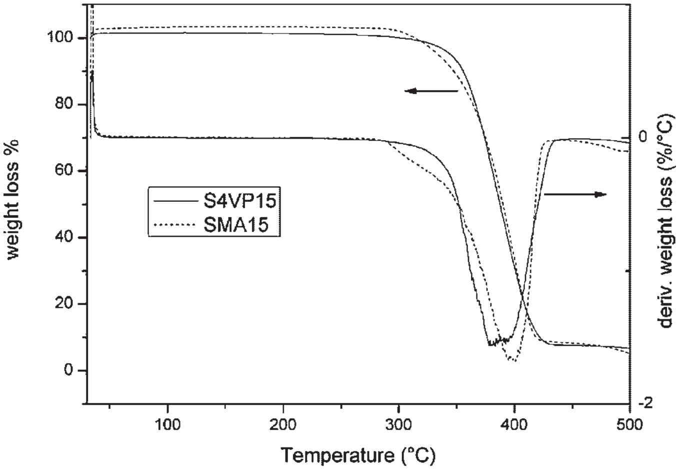


Figure 1.
TGA and *d*TGA curves of the SMA15 and S4VP15.

spectral resolution of 1 cm^{-1} and 64 scans were signal averaged.

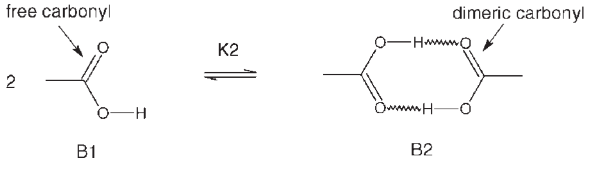
Theoretical Background

At a temperature above the glass transition temperature, the competing dynamic equilibria between the specific groups in SMA15/S4VP15/SAD17 blend system can be depicted by the Scheme 1–3 below:

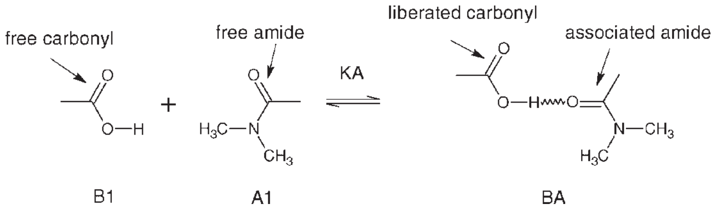
Free carboxylic acid groups (B_1) are assumed to self-associate in a cyclic dimeric form (B_2) and inter-associate both with free amide groups (A_1) to form a 1:1 complex (BA) and with free pyridine groups (C_1) to form 1:1 complex (BC).

According to the association model, described in detail in the monograph of Coleman *et al.*[11], the self-association equilibrium constant (Scheme 1) is given by:

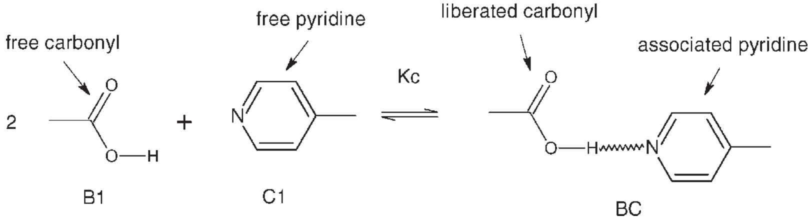
$$K_2 = \frac{\phi_{B_2}}{\phi_{B_1}^2}\left[\frac{1}{2}\right] \quad (1)$$



Scheme 1.



Scheme 2.



Scheme 3.

The inter-association equilibrium constant (Scheme 2) is given by:

$$K_A = \frac{\phi_{BA}}{\phi_{B_1}\phi_{A_1}}\left[\frac{r_A}{1 + r_A}\right] \qquad (2)$$

And the inter-association equilibrium constant (Scheme 3) is given by:

$$K_C = \frac{\phi_{BC}}{\phi_{B_1}\phi_{C_1}}\left[\frac{r_C}{1 + r_C}\right] \qquad (3)$$

The stoichiometry of the system is given by

$$\phi_{B_1} + \phi_{B_2} + \phi_{A_1} + \phi_{BA} + \phi_{C_1} + \phi_{BC} = 1 \qquad (4)$$

$$\Phi_B = \phi_{B_1}\left[1 + \frac{K_A\phi_{A_1}}{r_A} + \frac{K_C\phi_{C_1}}{r_C}\right] + 2K_2\phi_{B_1}^2 \qquad (5)$$

$$\Phi_A = \phi_{A_1}(1 + K_A\phi_{B_1}) \qquad (6)$$

$$\Phi_C = \phi_{C_1}(1 + K_C\phi_{B_1}) \qquad (7)$$

Where ϕ_i, Φ_i and $r_{A \text{ or } C}$ are the volume fraction of the polymer segment containing the i species, volume fraction of interacting polymer in the blend and the ratio of the molar volumes $V_{A \text{ or } C}/V_B$, respectively. The index B and A relates to self-associated polymer (B) which can inter- associate both with polymer (A) and polymer (C), respectively.

As the specific groups are diluted in styrene co-monomer, equilibrium constants can be transferred to a standard value by the relation:

$$K^{copolymer}V_B = K^{std}100 \qquad (8)$$

100 cm^3 is taken as a standard volume.

The Painter-Coleman association model describes the free energy of mixing of ternary polymer blends when strong specific interactions are present by the following expression:

$$\begin{aligned}\frac{\Delta G_M}{RT} = {} & \frac{\Phi_A}{M_A}\ln\Phi_A + \frac{\Phi_C}{M_C}\ln\Phi_C \\ & + \frac{\Phi_B}{M_B}\ln\Phi_B + \Phi_A\Phi_B\chi_{AB} \\ & + \Phi_C\Phi_B\chi_{CB} + \Phi_A\Phi_C\chi_{AC} \\ & + \frac{\Delta G_H}{RT}\end{aligned} \qquad (9)$$

The Flory-Huggins parameter χ is given by

$$\chi = (\delta_A - \delta_B)^2\frac{V_{ref}}{RT} \qquad (10)$$

Where δi is the solubility parameter that can be determined by group molar contribution.

The term $\frac{\Delta G_H}{RT}$ is the favourable contribution to the change in the free energy of mixing due to the presence of intermolecular hydrogen bonding interactions and is given by

$$\begin{aligned}\frac{\Delta G_H}{RT} = {} & \Phi_B\ln\left(\frac{\phi_{B_1}}{\phi_{B_1}^0}\right) + \frac{\Phi_A}{r_A}\ln\phi_{A_1} + \frac{\Phi_C}{r_C}\ln\phi_{C_1} + \Phi_B\left\{\left[K_2\left(\phi_{B_1} - \phi_{B_1}^0\right)\right] + \left[(1 - K_2\Phi_{B_1})\left(\frac{\xi+\zeta}{1+\xi+\zeta}\right)\right]\right\} \\ & - \left[\left(1 - K_2\phi_{B_1}^0\right)\Phi_B\ln\Phi_B + \frac{\Phi_A}{r_A}\ln\Phi_A + \frac{\Phi_C}{r_C}\ln\Phi_C\right]\end{aligned} \qquad (11)$$

Where $\zeta = K_A\Phi_{A1}/r_A \quad \xi = K_A\Phi_{A1}/r_A$

The criteria for thermodynamic stability for ternary polymer mixtures are given by:

$$\frac{\Delta G_M}{RT} < 0,\ \frac{\partial^2(\Delta G_M)}{\partial^2\Phi_A} > 0 \text{ and } \left[\frac{\partial^2(\Delta G_M)}{\partial^2\Phi_A}\right]\left[\frac{\partial^2(\Delta G_M)}{\partial^2\Phi_B}\right] - \left[\frac{\partial^2(\Delta G_M)}{\partial\Phi_A\partial\Phi_B}\right] > 0 \qquad (12)$$

Results and Discussion

Thermal Analysis

We have in a first step, carried out a DSC analysis for the three different SMA15/SAD17, SMA15/S4VP15 and S4VP15/SAD17 binary blends and confirmed their miscibility from the single glass transition temperature. The miscibility of SMA15/SAD17 and SMA15/S4VP15 is mainly due to the specific interactions that occurred between the carboxylic acid groups and the pyridine and carbonyl amide groups, respectively. As it can be seen in Figure 2 that shows the variation of T_g of the blend with SMA15 composition for these binary systems, positive deviations from linear average line were observed with all these blends.

A simplified form of the well-known Kwei equation, for a binary blend, was used to estimate the specific interactions that occurred within these blends from the constant q obtained from:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q\, w_1\, w_2 \qquad (13)$$

Where w_i and T_{gi} are the weight fraction and glass transition temperature of the i constituent.

The Kwei constant q measures the strength of the specific interactions.

The obtained q values shown in Figure 2 confirm that stronger interactions occurred within the SMA15/S4VP15 blends between the carboxylic and the pyridine groups. The Kwei constant obtained with the SMA15/SAD17 is in good agreement with that previously reported for blends composed of poly(styrene-co-acrylic acid) containing 18 mol% of acrylic acid and the same SAD17.[12]

The T_g of S4VP15 and SAD17 are very close. A single T_g varying with the composition and slightly higher than the linear average line with these blends, indicates the presence of very weak interactions compared to the blends above.

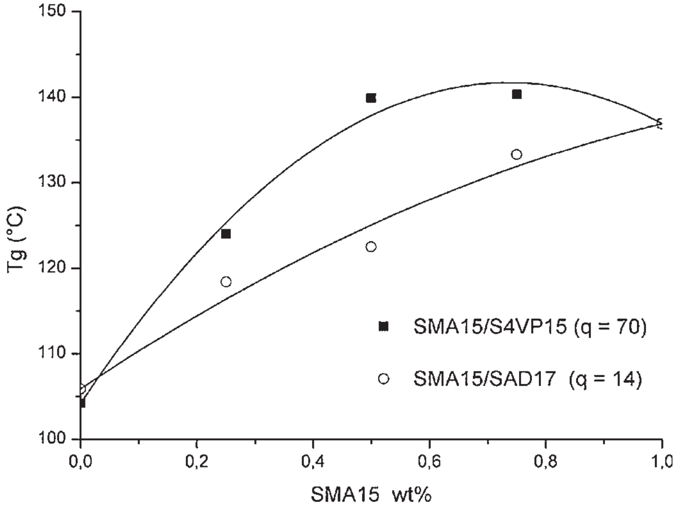


Figure 2.
T_g-composition of the binary blends.

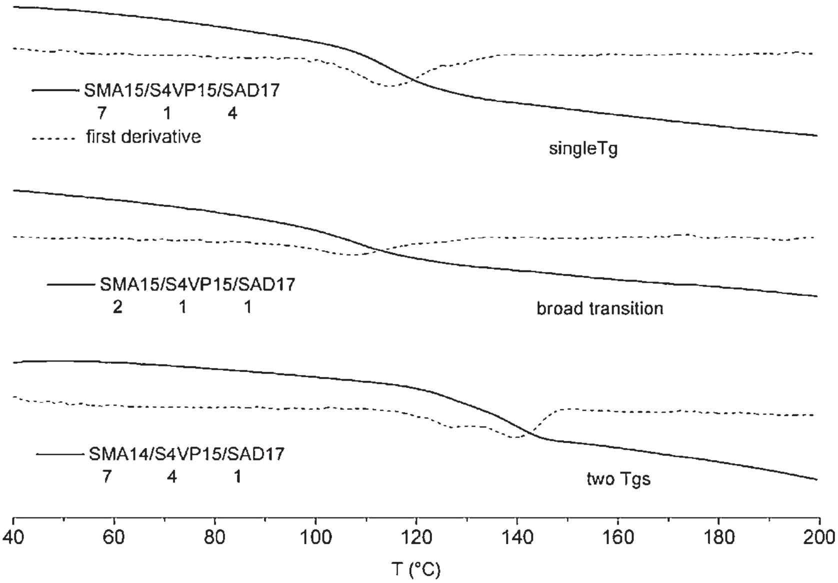


Figure 3.
Selected thermograms of SMA15/S4VP15/SAD17 blends.

Figure 3 shows selected second scan DSC thermograms of SMA15/S4VP15/SAD17 ternary blends with various compositions. Different miscibility behaviour is observed with these ternary polymer blends.

Depending on the blend composition, a single T_g or two T_gs are observed. A single Tg increasing with SMA15 content is observed with ternary blends containing a constant ratio of S4VP15/SAD17 equal or higher than 1:1. The ternary 4/7/1 and 7/4/1 blends are among those that exhibited two T_gs indicating that phase separation occurred. Their two phases are composed of miscible binary blends. Due to the stronger interactions that occurred within the SMA15/S4VP15 blends, the phase of high T_g contains mostly SMA15 and S4VP15.

Assuming that no hydrogen bonding interactions occurred between S4VP15 and SAD17 the modified Kwei equation below[13] was used to describe the ternary blend:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + w_3 T_{g3} + q_{12}\, w_1\, w_2 + q_{13}\, w_1\, w_3 \quad (14)$$

The values of the experimental T_g obtained by DSC and those calculated from the equation above and the well-known Fox relation are summarized in Table 2. As illustrated in Figure 4, the predicted values using the modified Kwei equation are in a fair agreement with those obtained experimentally.

Figure 5 displays a triangular phase diagram of the ternary polymer blend based on the DSC analyses.

FTIR Analysis

FTIR spectroscopy was first used to confirm the presence of the specific interactions that occurred within the blends between the acidic copolymer SMA15 and basic S4VP15 or SAD17 copolymers in the region where significant changes were observed. Figure 6 shows as an example the FTIR spectra of SMA15/SAD17 and SMA15/S4VP 1:1 ratio blends recorded at room temperature in the 1800–1550 cm^{-1} region. For brevity, the spectra of the other blends are not shown here. The FTIR spectrum of the SMA15/S4VP15 blend shows in Figure 6 in the 1650–1550 cm^{-1},

Table 2.
Experimental and predicted T_gs

Blend ratio			T_g exp	ΔT_g	T_g lin	T_g Fox	T_g Kwei
SMA15	S4VP15	SAD17	°C	°C	°C	°C	°C
0	1	0	104	9	104	104	104
0	0	1	106	9	106	106	106
0	1	3	106	16	105	105	108
0	1	1	110	11	105	105	109
0	3	1	109	13	105	105	107
1	1	10	**102**	16	108	108	111
1	4	7	101	12	108	107	113
1	7	4	104	16	107	107	114
1	10	1	**116**	25	107	106	113
1	1	4	105	17	111	110	116
1	4	1	110	18	110	109	120
2	5	5	105	18	110	109	119
1	0	3	118	14	114	112	116
1	3	0	124	24	112	111	125
1	1	2	96	20	113	112	121
1	2	1	**114**	26	113	111	124
1	1	1	**111**	20	116	114	126
4	1	7	110	14	116	114	121
4	7	1	137 . . . 120	25	115	113	–
5	2	5	**123**	14	119	117	127
5	5	2	130 . . . 116	22	118	116	–
1	0	1	123	17	121	119	125
1	1	0	140	11	121	118	138
2	1	1	**108**	21	121	119	132
7	1	4	114	19	124	122	130
7	4	1	140 . . . 127	19	123	121	–
4	1	1	141	22	126	124	136
3	0	1	133	18	129	128	132
3	1	0	140	13	129	127	142
10	1	1	137	17	132	130	137
1	0	0	137	7	137	137	137

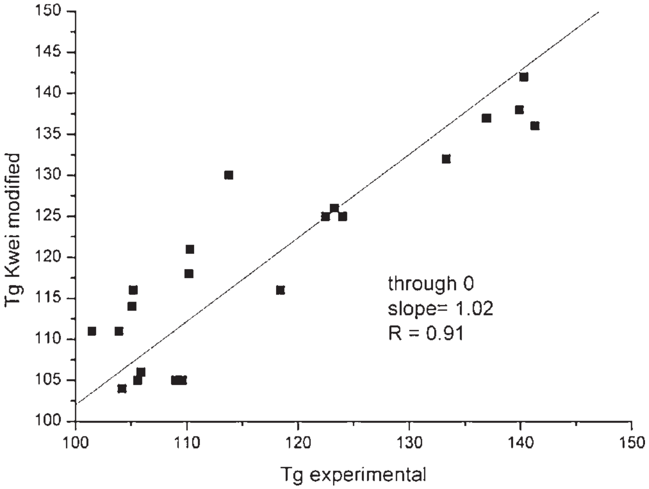


Figure 4.
Tg exp-Tg predicted by modified Kwei equation.

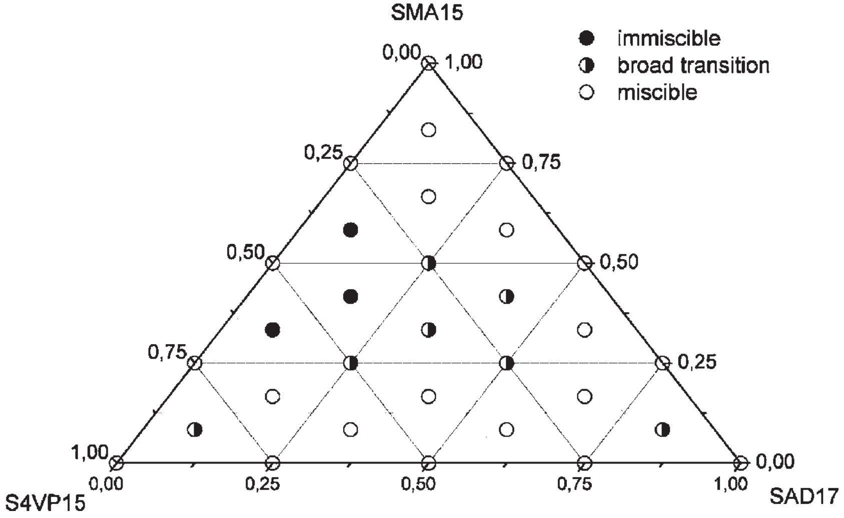


Figure 5.
Experimental phase diagram.

three contributions at 1597 cm^{-1}, 1607 cm^{-1} and 1638 cm^{-1}, attributed to free pyridine ring, hydrogen bonded pyridine "associated" and pyridinium cation, respectively. Similar band were reported in the literature.[14] SMA15 develops specific interactions with both S4VP15 and SAD17 as evidenced by the appearance of new bands as illustrated in Figure 6. Qualitatively, stronger interactions occurred between the carboxylic groups of SMA15 and 4-vinylpyridine of S4VP15 as illustrated in the figure above that compares the 1:1 ratios of these two binary blends from the high fraction of dimers observed with the SMA15/SAD17 blends and the presence of partial ionization that occurred at 1638 cm^{-1} with the other system.

We have carried out a quantitative analysis and calculated the equilibrium self-association constant for the acidic copolymer K_2 and its inter association constant with 4-vinylpyridine K_C[4] and with *N,N*-dimethylacrylamide K_A.[12]

The DSC results are in good agreement with those obtained in previous studies and confirm from the K_C value larger than K_A that stronger interactions occurred within the SMA15/S4VP15.

The values of these constants, together with the different parameters such as molar volume, solubility parameters that were used to calculate the free energy of mixing and phase diagrams for these ternary systems using the PCAM are given in Table 3.

Figure 7 shows the phase behaviour of this ternary system using the Painter-Coleman association model that predicts an immiscibility closed loop in a fair agreement with the variation trend of the experimental T_g values determined by DSC shown in the phase diagram of Figure 4 even in the presence of partial ionization of pyridine.

Figure 8 displays, as an example, the FTIR spectra of some of these ternary blends reflecting the different phase behaviours.

The fractions of the different species involved in these ternary blends through the various specific interactions were calculated using adequate curve fitting procedures. Due to the significant overlapping of the numerous specific interactions that occurred within the ternary blends, adequate band separation is rather very difficult to process particularly in the 1680–1550 cm^{-1} region as illustrated in Figure 9.

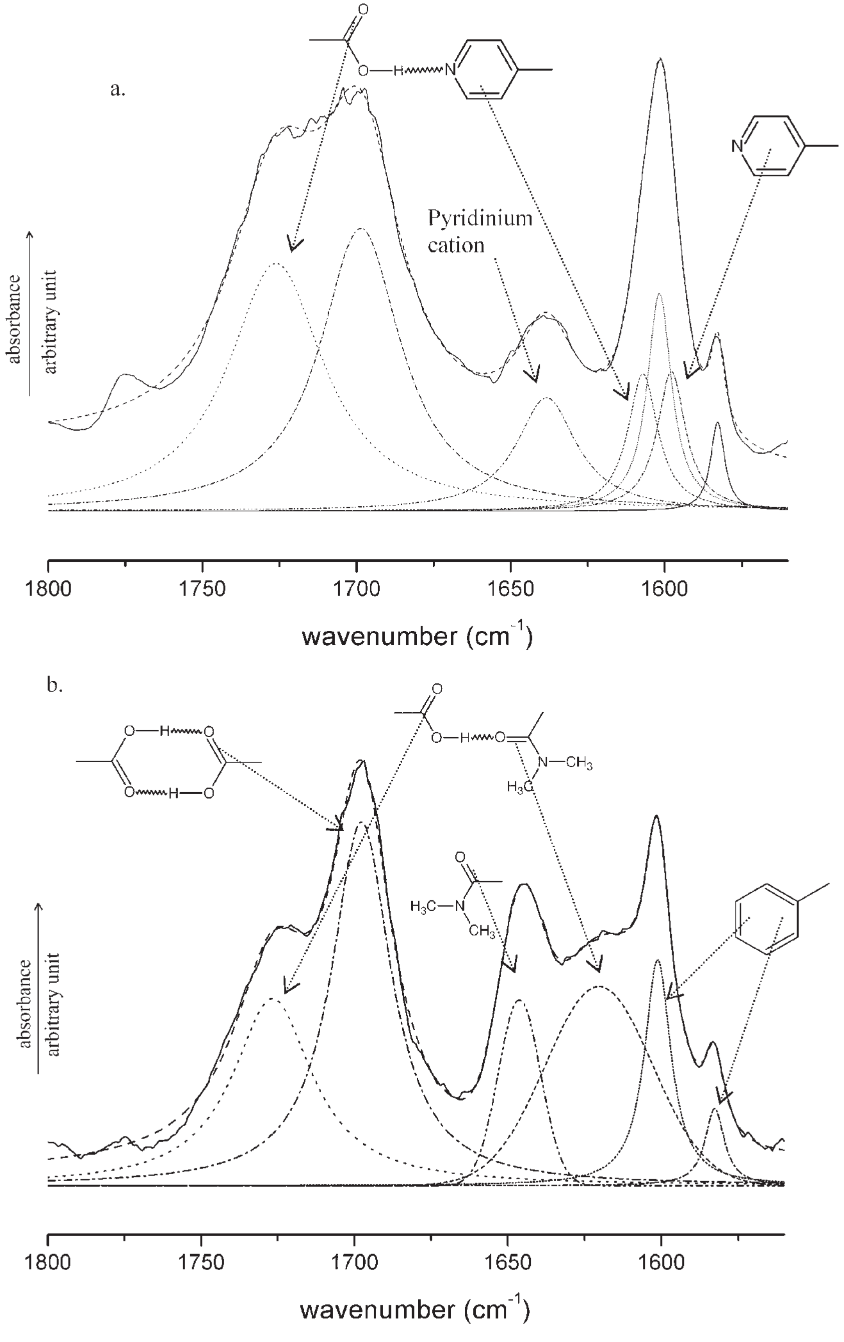


Figure 6.
FTIR spectra of SMA15/S4VP15 blends (a) and of SMA15/SAD17 blends (b).

A semi-quantitative analysis was carried out only in the carbonyl 1800–1650 cm^{-1} region. For a constant 1:1 ratio of the binary S4VP15/SAD17, the fraction of free carbonyl groups of the SMA15, increased with the SMA15 content. Figure 9 confirms the

Table 3.
Thermodynamic parameters

Copolymers	Molar volume	Solubility parameters	Equilibrium constants
	$cm^3 \cdot mol^{-1}$	$(cal \cdot cm^{-3})^{0.5}$	
SMA15	597	9.635	$K_2 = 163$
S4VP15	617	9.695	$K_C = 1300$
SAD17	547	9.534	$K_A = 200$

presence of the different species due to the specific interactions that occurred within the ternary blends. The intensity of such interactions was found to vary with the blend composition and the corresponding phase separation of the 4/7/1 and the miscibility of the 4/1/7 blends in a good agreement with both the experimental DSC study and the theoretical prediction using the Painter-Coleman association model.

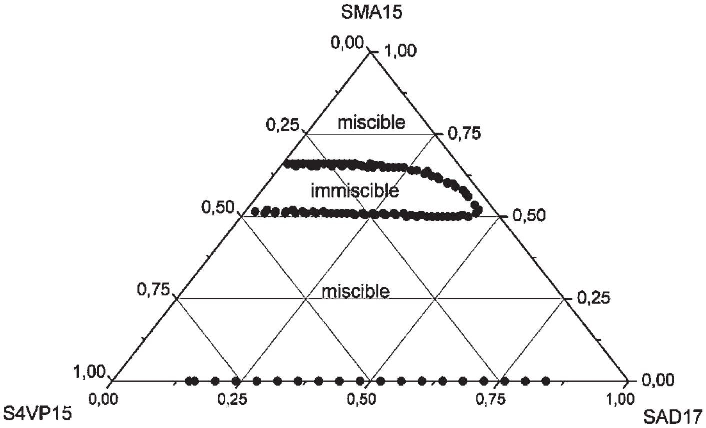


Figure 7.
Ternary phase diagram calculated using the Painter-Coleman association model.

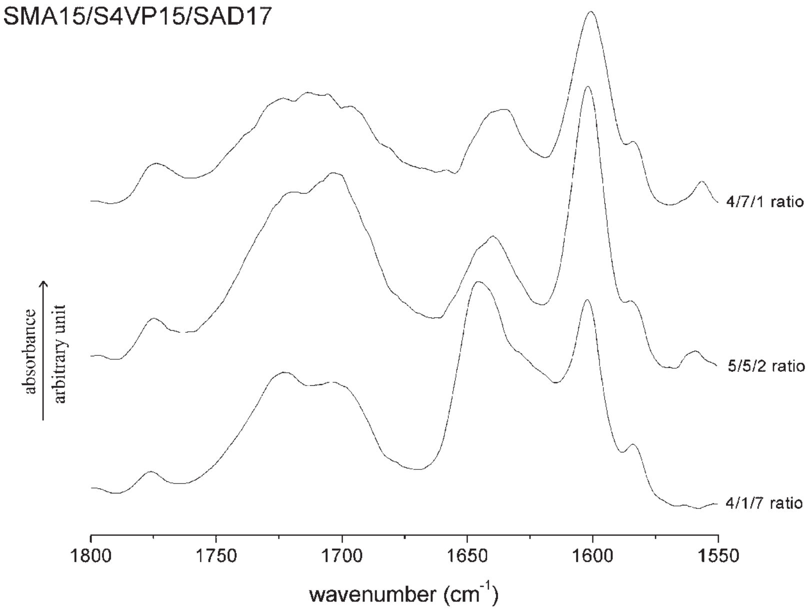


Figure 8.
FTIR spectra of selected SMA15/S4VP15/SAD17 ternary blends in the 1800–1550 cm^{-1} region.

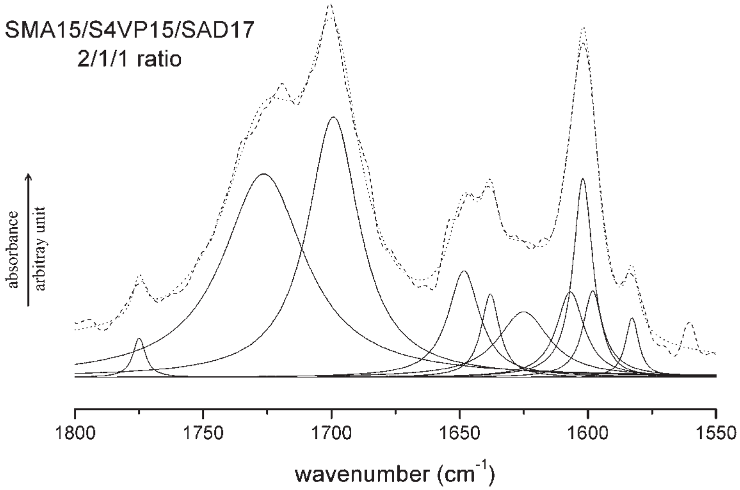


Figure 9.
Illustration of expected curve fitting of SMA15/S4VP15/SAD17 2/1/1 ternary blend.

Conclusion

The phase behaviour of the ternary system, poly(styrene-*co*-methacrylic acid) containing 15 mol% of methacrylic acid (SMA15), poly(styrene-*co*-N,N-dimethylacrylamide) containing 17 mol% of N,N,-dimethylacrylamide (SAD-17) and poly(styrene-*co*-4-vinylpyridine) containing 15 mol% of 4-vinylpyridine, was studied by both DSC and FTIR spectroscopy. The results showed that this blend exhibits only partial miscibility with a closed loop of immiscibility even though the binary polymer pairs composed of any two of these three constituents were miscible. This is due to the significant difference in the strength of the interactions that SMA15 developed with S4VP15 and SAD17, respectively. The use of the Painter-Coleman association model to this ternary system, in which both partial ionization and hydrogen bonding interactions occurred, seems to predict fairly well the observed phase behaviour analyzed by DSC.

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